

Discharges from Coal Gasification Plants

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16. ABSTRACT The paper reviews organics data obtained from fixed-bed coal gasification processes. The review indicates that, when gasifiers were operated with fuels having similar volatiles contents, they all produced about 30 kg of condensable organics per metric ton of feed coal; entrained-bed processes produced virtually none. These condensable organics were generally similar in composition. However, detailed comparisons of the results indicated that the sums of the speciated components accounted for a relatively small portion of the total organics and that significant data gaps remain. Further investigation indicated that the speciation methodology may have omitted certain types or classes of compounds that were not specifically sought. This review points up the strengths and identifies weaknesses in the data compilations.		
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Discharges from coal gasification plants

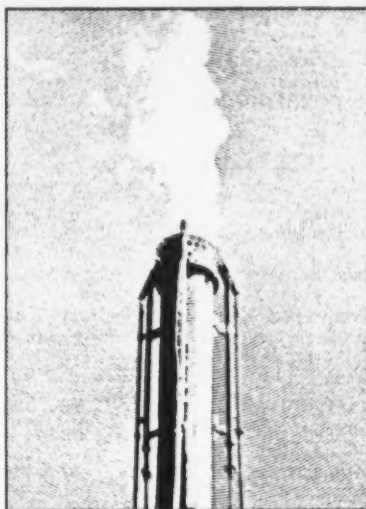
Data on organics were obtained from a survey of 12 fixed-bed test sites

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During the past decade intense efforts have been made to find alternative sources of clean energy and to develop and evaluate coal gasification processes. Some of these efforts have been devoted to assessing environmental effects. Researchers soon realized that the volumes of engineering data accumulated during the many decades of coal gasification research were not directly applicable to environmental questions and that new data were needed.

Consequently, a program was developed to conduct numerous tests on product, process, and waste discharge streams from several coal gasification facilities, including commercial, pilot, and process development units. Conducted under the sponsorship and direction of the Air and Energy Engineering Research Laboratory of EPA, these investigations varied in scope and dealt with a range of pollutants, with special emphasis placed on organic compounds. Data from these tests may be found in numerous reports and symposia proceedings (1-20).



sia proceedings (1-20).

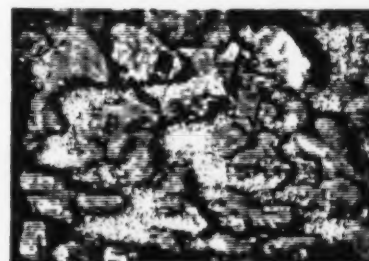
Because data from several test sites are distributed throughout more than one document, several documents must be consulted to obtain a comprehensive picture of any pollutant concern related to any one gasifier. Recently, organics data from 12 test sites (Table 1) were consolidated into a single report that facilitates an interpretive evaluation of the organics data (21). We will discuss these combined organics data in light of the methodologies that were used to obtain them and will examine some inherent limitations of these data. Such limitations should be understood by those who use these data to estimate the potential environmental effects of a gasification process or to select a pollution control scheme for treating a gasifier discharge.

Test methodology

The methods for sampling and analysis were test-specific, but the same basic techniques were used throughout the program. Solid and liquid samples usually were collected by established methods for obtaining representative point-in-time samples, and gases and vapors

normally were collected by a sampling train that was adapted specifically for each situation. Gas stream sampling was most complex and accounted for a major portion of the sampling effort. Several types of organics data were generated by these source tests: bulk organics loading in which volatile organics (VO) were determined by gas chromatography and nonvolatile organics (NVO) were determined gravimetrically (22); detailed analyses using gas chromatography/mass spectrometry (GC/MS) (3, 11); water quality parameters pertaining to the organic content of aqueous streams and leachates from solid wastes (23); and fingerprints provided by GC and IR spectrometry (24).

Bulk organics loading determinations accompanied by a liquid chromatographic fractionation—known as the survey method—were used most widely and provided the most useful basis for comparing the organics produced by the tested processes (22). Detailed analyses by GC/MS were performed on samples from two of the 12 test sites: Holston, which uses the Chapman/Wilputte process, and the University of Minnesota at Duluth, which uses Foster Wheeler/STOIC Combustion Ltd. (FW/STOIC). At several test sites, detailed analyses were limited to testing for "criteria pollutants"; therefore, only listed identifier compounds (compounds on the list of



criteria pollutants) were sought and their concentrations were determined. All other compounds were ignored. In this study, criteria pollutant analyses were of limited value in comparing processes for pollution potential because reliable identifiers for gasification sources had not been identified at the time of testing.

Test results

Concentrations of bulk organics in the major discharge streams of several fixed-bed gasifiers, as obtained by the survey method, are reported in terms of both concentration and mass flow (Table 2). Organics production also is

expressed in terms of coal consumed so that comparisons can be made between gasifiers that have different production capacities.

Organics in the crude product gas from fixed-bed gasifiers are produced largely from the thermal devolatilization of coal. Consequently, all tar-producing gasifiers, when operated on coals having similar volatiles contents (40%), produced approximately the same mass of condensable organics (30 kg) per metric ton of coal consumed. In contrast, when operated on anthracite with 5% volatiles, the fixed-bed gasifier at Glen Gery produced organics at a much lower rate (0.04 kg/

metric ton). Similarly, the bottom gas from the two-stage (FW/STOIC) unit that gasifies previously devolatilized coal is virtually free of organics and therefore produces organics at a rate that is well below the norm for fixed-bed gasifiers operating on high-volatiles fuels.

The entrained-bed processes, which include the Texaco, Kellogg-Rust/Westinghouse (KRW), and Koppers-Totzek processes, force the volatilized organics through the gasification zone, where they are converted to hydrogen and carbon monoxide. Consequently, the product gases contain a lower concentration of condensable organics. Because the

TABLE 1
Test sites in the organics characterization program

Plant	Gasification process	Fuel	Type operation
Fort Snelling (MN)	Wellman-Galusha (low Btu)	ND lignite	a
Glen Gery (York, PA)	Wellman-Galusha (low Btu)	Anthracite	b
Holston (Kingsport, TN)	Chapman/Willputte (low Btu)	Bituminous coal	b
Kosovo (Pristina, Yugoslavia)	Pressurized, fixed-bed gasifier	Lignite	b
Modderfontein (South Africa)	Koppers-Totzek entrained-bed	High volatile bituminous coal	b
Ptolemais (Greece)	Koppers-Totzek entrained-bed	Bituminous coal	b
Worcester (MA)	Riley gas producer (low Btu)	Lignite	a
Oberhausen-Holten (West Germany)	Texaco entrained-bed	IL no. 6 bituminous coal	c
Duluth, University of Minnesota	Foster-Wheeler/STOIC (low Btu gasifier)	Lignite	a
Madison, PA	Kellogg-Rust/Westinghouse, fluidized-bed process development unit	WY Subbit. coal Pittsburgh #8 Bituminous coal ND lignite	a
Other Programs			
Homer City (PA)	BI-Gas Pilot Plant	Pittsburgh #8 bituminous coal	a
SASOL (South Africa)	Lurgi Mark IV (modified)	KY #9 bituminous coal	b

a: Test process, no longer in operation.

b: Commercial/industrial process—operated prior to this program and is still operating.

c: Commercial unit that performs tests on demand.

TABLE 2
Summary of organics data from six fixed-bed gasifiers

Units	FW/STOIC (Duluth)	Wellman-Galusha (Ft. Snelling)	Riley (Worcester)	Chapman (Holston)	Lurgi type (Kosovo)	Wellman-Galusha (Glen-Gery)
Coal type	Lignitic	Lignitic	Lignitic	Bituminous	Lignitic	Anthracitic
Volatiles	37	42	42	37	40	5
Coal feed rate	g/sec 270	250	670	300*	4400	220
Dry gas flow rate	m ³ /sec 1.0	0.55	2.2	0.87	5.6	1.2
Product gas—concentration	g/m ³ 4.0	16	9.1	24	7.7*	0.0070
mass flow	g/sec 3.8	8.6	8.0	1.0*	7.8*	0.0084
Gasifier ash—concentration	g/kg 0.10	0.64	0.24	0.018	0.40	0.12
mass flow	g/sec 0.0035	0.015	0.018	0.00033	0.31	0.002
Cyclone dust—concentration	g/kg 0.10	13	5.6	0.38	—	0.78
mass flow	g/sec × 10 ⁴ 0.10	4.9	220	6.1	—	1.5
Ash Q-water—concentration	g/L 0.0013	0.13	0.012	—	—	0.046
mass flow	g/sec 0.09	<9.0	260	—	—	—
Tar/oil by-products—mass flow	g/sec 3.7	—	14	17	200*	—
Plant total—mass flow	g/sec 7.5	8.7	22	18	210	0.110
Total per metric ton of coal	kg/metric ton 28	35	33	60	47	0.045

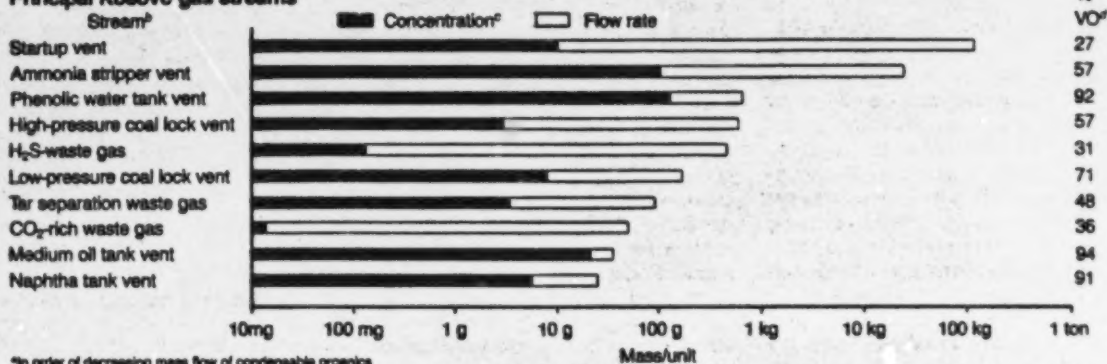
*Gasifiers operating in parallel.

*Based on concentration at low-pressure coal lock vent.

*Based on organic concentration in gas at coal feeder vent.

*Based on total mass of by-products plus organics discharged to waste.

FIGURE 1
Principal Kosovo gas streams^a



^aIn order of decreasing mass flow of condensable organics

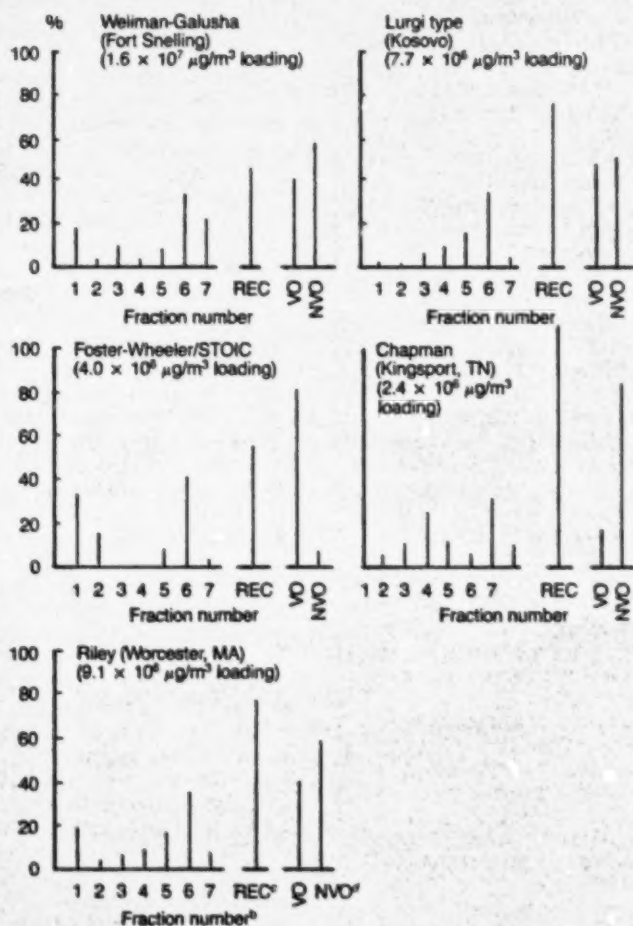
^bNot shown: tar tank vent, which discharges 8 g/h at a flow rate of 0.55 m³/h

^cThe scale for concentration is mass/m³ measured from the ordinate, and the scale for mass flow rate is mass/h. The volumetric flow rate is m³/h measured from unity. For example, the ammonia stripper vent concentration is about 100 g/m³, the mass flow is 24 kg/h, and the volumetric flow is 240 m³/h.

^dVO = Volatile organics

Source: Reference 20.

FIGURE 2
Comparison of organics in product gas^a



^aFrom several fixed-bed gasifiers.

^bPercent eluted in each liquid chromatography fraction.

^cPercent recovered from liquid chromatography.

^dPercent volatile and percent nonvolatile organics.

Source: Reference 21.

survey analyses were not used to measure organics loadings of these product gases, a rigorous comparison of these processes with fixed-bed processes cannot be made. Nevertheless, the differences in organics loading between these and fixed-bed processes are so great that juxtaposed organics data from the two groups are informative even though the data were obtained by different methods. For example, a total organics loading for the KRW product gas was on the order of 1 g/ton of coal, which is 0.003% of the level of condensable organics in product gas from the fixed-bed gasifiers.

The total organics loading value for the KRW product gas was obtained by adding the concentrations of the individual organic species as determined by GC/MS, rather than by the survey method that was used with fixed-bed gasifiers. Because the total organic values obtained by adding the concentrations of each species usually represent only a portion (10–50%) of the total organics as determined by the survey method, the KRW result may be low. The difference between 10% and 0.003%, however, is so great that it indicates a real difference between the two types of gasification processes in terms of organics produced. In support of this conclusion, the condensable organics produced by the KRW gasifier were dominated by benzene. On the other hand, the organic masses produced by the fixed-bed gasifiers were dominated by tar and medium-boiling-range oil, both of which represented about 75% of the organic mass. Organic loadings of the gasifier ash from the fixed-bed gasifiers were all between 100 mg/kg and 600 mg/kg of coal feed, except for ash from the Chapman unit, which had loadings of 18 mg/kg.

A plant-wide survey of a commer-

cial facility. The most comprehensive survey of this program was conducted at the Kosovo plant, where 21 streams were characterized. The Kosovo facility operates six oxygen-blown pressurized gasifiers and uses gas-cleaning (Rectisol), quench-water separation (tar separation), and quench-water extraction (Phenosolvan) processes. A survey of the organics loadings in 11 significant streams (Figure 1) indicates the potential for organic pollution by these processes. Figure 1 indicates both stream concentrations in g/m³ and mass flow in g/h on a logarithmic scale. The abscissa beginning at unity (1) also may be used as a scale to indicate a stream's flow rate in m³/h.

Organic profiles by liquid chromatography (LC). Information about the organics loadings in the discharges from a source is valuable because it indicates a potential for pollution from that source. Loading data can be obtained in a cost-effective manner, but its usefulness is limited because it provides no information about the chemical composition of the organics being discharged. To supply that information, the survey analysis included a simple method for obtaining a profile of the organics (22).

To obtain a profile, organics were separated into seven fractions by column chromatography using a silica gel packing and an elutropic series, which

is a sequence of eluting solvents of increasing polarity. Although the seven categories defined by the elutropic series are entirely empirical and the same compound or class of compounds may be found in more than one fraction, the profile provides a useful description of the condensable organics that are generated and transported in these processes. Typical fractionation results of the organics in crude product gas streams of five fixed-bed gasifiers are compared in Figure 2. Also shown are the distributions of volatile and nonvolatile organics and the percentage of the total organics recovered from the chromatographic procedure. Comparing the respective graphs indicates the following:

- The organics from all five of the tested gasifiers contain a significant portion of polar organics (most likely phenols and pyridines) in fraction 6.
- The organics from several gasifiers contain a significant portion of nonpolar organics. It is likely that these nonpolar organics, fraction 1, are either paraffinic hydrocarbons or alkylated aromatics.
- Recoveries from LC average 77 ± 27%. The value at the Chapman unit, however, was greater than 100%, which casts some doubt on the validity of that profile. A large amount of material in and around fraction 4 is typical of phthalate plasticizers, which are relatively common laboratory contaminants.
- The distributions of VO and NVO from the depicted processes do not follow a uniform pattern. For example, the Chapman organics from bituminous coal show high levels of NVO, but the organics from three gasifiers using lignite (Riley, Wellman-Galusha Fort Snelling [WG-FS], and Kosovo) show nearly equal proportions of VO and NVO. On the other hand, the organics from the combined gas of the two-stage FW/STOIC gasifier, which also used lignite, do not follow this type of uniform pattern.

The FW/STOIC combined product gas is not simply top dirty gas combined with the comparatively clean bottom gas. Rather, the two streams, top and bottom, are combined after tar and oil aerosols have been removed from the top dirty gas by an electrostatic precipitator (ESP). Consequently, the organics in the combined gas are those that have passed through the ESP as vapor and consist primarily of VO.

By-product tars and oils. By-product tars and oils, characterized by the survey method, provided useful data against which other LC, VO, and NVO results could be compared. Because the tars originate in the gasifier and are

Organics in solid and liquid discharges

The organics from solid and liquid discharges (e.g., gasifier ash, cyclone dust, and quench liquor) from the plants surveyed were evaluated by the same method used for the organics in product gas. Several observations were made:

- **Gasifier ash.** The extracted organics from all tested ashes (at WG-FS, FW/STOIC, and Riley) show nonpolar hydrocarbons, LC fraction 1, as the largest fraction. The VO-NVO distribution pattern, however, is not uniform between the tested gasifiers. The WG-FS and Riley organics consist primarily of NVO (a 95:5% ratio), whereas the FW/STOIC organics contain less VO than NVO (a 30:70% ratio). Organics loadings of the tested ashes were 0.6 g/kg for WG-FS, 0.1 g/kg for FW/STOIC, and 0.24 g/kg for Riley.
- **Cyclone dust.** Organics extracted from the cyclone dusts all show similar VO-NVO ratios (5:95%) and chromatographic distributions with fractions 1 and 6 as major fractions. The organics extracted from the WG-FS dust, however, show a moderate amount of material in fractions 3, 4, and 5, indicating possible contamination by organic plasticizers. The extractable organics loadings of the tested dusts were 13 g/kg for WG-FS, 5.6 g/kg for Riley, and 0.38 g/kg for Chapman. The higher organics loading value of the WG-FS dust may be attributed, in part, to contamination by organic plasticizers that increased LC fractions 3, 4, and 5.
- **Gas quench liquor.** Organics extracted from quench liquors from two gasifiers, Kosovo and Chapman, show similar VO-NVO ratios (30:70%). LC profiles of the extracted organics from both sources show large amounts of material in the polar fractions, attributable to phenols and pyridines. The Kosovo samples, however, contain a nearly equal balance between polar and nonpolar material, but the Chapman organics contain very little nonpolar material. A Chapman liquor sampled at a later date corroborates the low level of nonpolar material. The liquor was subjected to an acid-base-neutral extraction, which indicated that the extracted organics from Chapman liquor contain 85% acid extractable compounds and 15% base-neutral compounds. Because the acid-extractable compounds included phenols and the base-neutral compounds included both pyridines and nonpolar hydrocarbons, it is evident that the level of nonpolar organics is less than 15% in the Chapman liquor. This result is in substantial agreement with that of the LC profile.

Recoveries from LC ranged between 70% and 100% for extracted organics from two Kosovo liquors and one Chapman liquor. Both Kosovo samples showed an organics loading of 11 g/L, and the Chapman sample showed a loading of 4.8 g/L. A Chapman liquor sampled at a later date showed a loading of 9.3 g/L, which is comparable to the Kosovo loading. Although the Chapman liquor is recirculated, the organics loading is not constant. Factors that may influence the organics loading are the composition of the coal volatiles, the coal moisture, and the frequency of blowdown.

Water quality parameters pertaining to organics from aqueous streams and solid leachates permit some comparisons among gasifiers (23). The water quality data indicate that gas liquors from fixed-bed processes that use highly volatile fuels transport significantly more organics than do other aqueous streams from gasification processes (Table 3).

transported by the product gas until separated, LC and VO-NVO distribution data should be consistent with the distribution profiles of organics in other streams.

The LC distributions of some by-product tars, however, do not support this premise. For example, the LC distribution of the tar from the Kosovo plant shows more nonpolar material than would be expected in the organics collected from its product gas. The LC distribution of Kosovo tar more closely resembles that of the organics from the product gases of the other tested gasifiers (e.g., Riley, WG-FS, or FW/STOIC). Because a significant quantity of nonpolar organics are removed from Kosovo organics as medium oil and naphtha, it is likely that the LC distribution of Kosovo tar is valid. It is also likely that the distribution of Kosovo organics shown in Figure 2 is not a true representation of the organics produced in the gasifier but is a representation of the emission from the low-pressure (LP) coal vent where that sample was taken. Test data from the FW/STOIC gasifier indicate that oil taken from the ESP is different from either Kosovo or Chapman by-product tars in that the ESP oil contains more nonpolar organics (fraction 1) than polar organics (fraction 6).

Benefits and limitations of the survey analyses data. The results of the survey analyses provide a useful basis for comparing the production and transport of organics in gasification processes. The method is simple and cost-effective. Although the resulting data are not species-specific, they provide useful information concerning the vola-

tility, polarity, and mass flow of organics. Only limited inferences, however, can be made about stream composition from these properties.

The major limitation of these survey results is that the quality of the data is method-dependent. Chromatographic and VO-NVO fractions that characterize the distributions of organics overlap, and mass measurements are subject to interferences by inorganic substances that also are soluble in the extracting solvents (e.g., S_8). Consequently, considerable judgment is needed to interpret the data, yet the method provides some inherent safeguards that flag invalid data. For example, a recovery greater than 100% (as in Chapman, Figure 2) clearly indicates that the LC distribution is suspect. A likely contaminant is phthalate plasticizer, which should elute around fraction 4. If a visual correction is applied to the Chapman distribution, a pattern resembling that of the Kosovo organics can be recognized.

Detailed organic analyses

In this program, the Chapman gasifier study provides the most thorough speciation for organics. Streams selected for detailed analyses at this facility were the coal feeder vent, the separator vent, the separator liquor, the separator tar, the gasifier ash, and the cyclone dust. A total of 111 compounds from 14 different classes of organics were identified and quantified in samples from the 6 streams (see box).

A data summary listing major components (Table 4) together with the list of identified chemical classes (Table 5) illustrate the character and complexity

of the organic mixtures associated with this gasification process. The actual number of components contained by the organics in these streams might be much larger than the number found by GC/MS. Many of the compounds identified have isomeric structures that could not be resolved. Moreover, many components are not sufficiently volatile to elute within the time and temperature constraints of the analysis and therefore would not be detected. Furthermore, there is clear evidence (2, 3) that the organics collected from the coal-feeder vent discharge do not reveal all of the components that occur in the hot product gas that transports the tar.

It can be assumed that all components found in these organics are produced in the gasifier. Some components, such as naphthalenes, phenols, and nitrogen-bearing heterocyclics, are found in the major organics-bearing streams—coal-feeder vent, separator vent, separator liquors, and tar. Many components found in separator liquor and separator vent gas are not found in the feeder vent gas, even though all of these components must have originated in the gasifier and are transported in the hot crude product gas. Two plausible explanations for the absence of these components from the feeder vent gas can be offered. First, the feeder vent gas was cooler than the crude product gas and therefore did not transport many of the higher boiling components. Second, the recycled liquor and the tar accumulate and therefore concentrate many components that are below the threshold of detectability in the vent gas organics.

The detailed analytical data indicate

TABLE 3
Water quality parameters of selected aqueous streams^a

Process	Stream ^b	Chemical oxygen demand (ppm)	Biological oxygen demand (ppm)	Total organic carbon (ppm)	Phenol (ppm)
Lurgi type (Kosovo)	Gas quench	18,900	9030	4970	2120
Chapman (Kingsport, TN)	Gas quench	22,000	6530	— ^c	—
Kellogg-Rust/	Gas quench	270	—	80	6
Westinghouse (Madison, PA)					
Texaco (Ruhrkohle)	Settler underflow	177 ± 29	315	195 + 100	<0.018
Koppers-Totzek (Modderfontein)	Settler underflow	4	4	5.3	—
Fixed-bed group ^d	Ash sluice	0.76-100	<1-90	0.3-16	0.006-0.36
Koppers-Totzek (Modderfontein)	Rectisol condensate	350	120	15	0.01
Lurgi type (Kosovo)	Phensolvan outlet ^e	7910	2350	1470	230
Wellman-Galusha (Fort Snelling, MN)	Cyclone dust	800	—	185	9.8

^aFrom gasification processes.

^bFor a rigorous identification of these streams and complete data, see Reference 22, Table 6.

^c— = no value available.

^dRange of values for the fixed-bed groups that include Wellman-Galusha-Fort Snelling, Foster-Wheeler/STOIC, Riley, Lurgi type (Kosovo), and Chapman.

^eExtracted water.

that the following take place:

- Gasifier ash and cyclone dust are essentially organics-free, totaling 4 μg and 13 μg of organics/g of sample, respectively.
- Only a limited number of components—naphthalenes, phenols, and quinolines—are common to all streams.
- Considerable fractionation occurs between tar, liquor, and vent gas in the separator, and these streams have few species in common.

The identified species account for only a portion of the total organics found by the survey method (Table 3). Their concentration varies from about 50% in the liquor to about 10% for the coal feeder vent gas and about 5% for the tar. Although the results are from a comparison of two independent samples, the levels and compositions have been judged sufficiently uniform to allow this comparison.

The major components in each organics-bearing stream are listed in Table 3. Major components are defined as those having concentrations equal to or greater than 10% of the sum of the determined species. Their concentrations indicate that a few species constitute a major portion of the identified mass. For example, three species make up 95% of the identified organics in the separator liquor, three other compounds comprise 56% of the identified organics in the coal-feeder vent gas, and six components (four in common with other streams) comprise more than 50% of the identified organics in tar. From these data, it is evident that the identified species provide a reasonable indication of the composition of the organics in separator liquor and separator vent gas in which a few dominant species with sufficient volatility for chromatography comprise about 40% of the mass. The identified species, however,

do not provide nearly as complete a description of the composition of those organics in the separator tar or in the tar-bearing coal feeder vent gas. There, identified species describe only 10% of the stream's mass, and of the 10%, about 5% of the mass is described by individual components.

A detailed analysis of organics from the FW/STOIC gasifier provided a similar result. In that study, the organics from five process streams and two combustion streams were analyzed by high-resolution GC/MS using a 30-m quartz capillary column at the same conditions for all samples. Although some peaks were identified specifically, many others were not. Because each peak of a chromatogram represents at least one component and no component can produce two peaks, the number of peaks on each chromatogram indicates a minimum number of components contained in each sample. A spread sheet can be used to compare the range of components in several streams when all components of all streams are entered in order of increasing gas chromatographic retention time. An internal standard of deuterium-labeled (D10) anthracene was used with all samples to convert peak areas to mass units relative to the internal standards. Thus each component could be quantified.

The organics from each stream contained the following minimum numbers of components: 139 for ESP oil, 134 for product gas, 108 for gasifier ash, 51 for cyclone dust, 32 for product gas combustion emissions, 31 for ash pan water, and 26 for ESP oil combustion emissions. The boiling range of the eluting compounds, as extrapolated from the retention of normal hydrocarbons, was 150–450 °C. As with the Chapman organics, the sum of the quantified components accounted for only a fraction (about 10%) of the total organics as determined by the survey method. About half (51% $\pm$ 20%) of the components eluted from the GC column have been identified by compound or compound class.

The major differences between the Chapman and the FW/STOIC results were the level of organics and the number of components found in the two gasifier solids, gasifier ash, and cyclone dust. The FW/STOIC ash had an organic loading 6 times that of the Chapman ash and contained at least 108 components amenable to chromatography, compared with six components for the Chapman ash. Many of the extracted components were long-chain paraffins. Similarly, the organics loading of the FW/STOIC cyclone dust was 4 times that of the Chapman dust and contained at least 51 components, compared with three components that were

TABLE 4
Summary of major components from Chapman gasifier

	Coal-feeder vent gas ($\mu\text{g}/\text{m}^3$)	Separator vent gas ($\mu\text{g}/\text{m}^3$)	Separator liquor ($\mu\text{g}/\text{L}$)	Tar ($\mu\text{g}/\text{m}^3$)
Total organics by survey	7.8×10^5	4.2×10^6	4.8×10^6	7.7×10^5
Sum of stream components by GC/MS	7.2×10^4	1.6×10^6	2.0×10^6	2.5×10^4
Major components ^a				
Naphthalene	10^4			
Methylnaphthalene	10^4			
Acenaphthalene				2×10^3
Methyl acenaphthalene	2×10^4			2×10^3
Phenanthrene/anthracene				2×10^3
Benzofluorene/methylpyrene				2×10^3
Phenol		3×10^5	6×10^5	
C ₁ -Alkyl phenol		5×10^5	10^6	2×10^3
C ₂ -Alkyl phenol		7×10^5	3×10^5	4×10^3
Sum of major components	4.0×10^4	1.5×10^6	1.9×10^6	1.4×10^4
Major components as % of sum of stream components	56	94	95	56
% major components relative to total organics by survey	5.1	36	40	1.8
% Speciated relative to total organics	9.2	38	42	3.2
Number of species determined	53	53	37	71

^aArtifacts of sampling and sample handling (plasticizers) were subtracted from total (3.6×10^4) to obtain values reported here.

^bComponents with concentration > 10% of sum of stream components.

TABLE 5
Compound classes identified

Chemical class	Representative compounds
Hydrocarbons	Alkanes, alkenes
Aromatic hydrocarbons	Benzene, alkylbenzene, hydrophthalene
Alcohols	Phenols, alkyl phenols, polyhydroxyphenols
Ethers	Anisoles
Ketones	Benzophenones
Amines	Anilines, aminoaphthalenes
Nitrogen heterocyclics	Pyridines, pyrroles, quinoline
Sulfur heterocyclics	Alkylthiophenes
Heterocyclics	Furans
Nitriles	Benzonitrile
Carboxylic acids	Phthalic acid
Esters	Phthalates, adipates
Polycyclics	Naphthalene, benzopyrene
Fused nonalternant polycyclics	Indene, fluoranthene

detected in the Chapman dust.

Because high-resolution capillary GC was used for the FW/STOIC mass spectrometric analysis and low-resolution, packed-column GC was used for the Chapman mass spectrometric analysis, allowance must be made for differences in analytical techniques between the two gasifiers. In addition, the extracts from Chapman solids (ash and cyclone dust) were severely contaminated with plasticizer, comprising about 75% of the eluting mass, that dominated the chromatogram and automatically suppressed the detectability of other organics that might have been present in smaller amounts but were not detected.

These detailed analyses were not intended to speciate the bulk compositions of these materials but rather to identify potentially hazardous compounds within 26 organic classes so that the potential environmental burden from these substances could be assessed. The quantifications were estimates and should not be used as quantitative statements of composition. The arithmetical treatment of the percentages shown has been included to stimulate an awareness of the limitations of these data rather than to provide a definitive statement of composition for the organics in these streams.

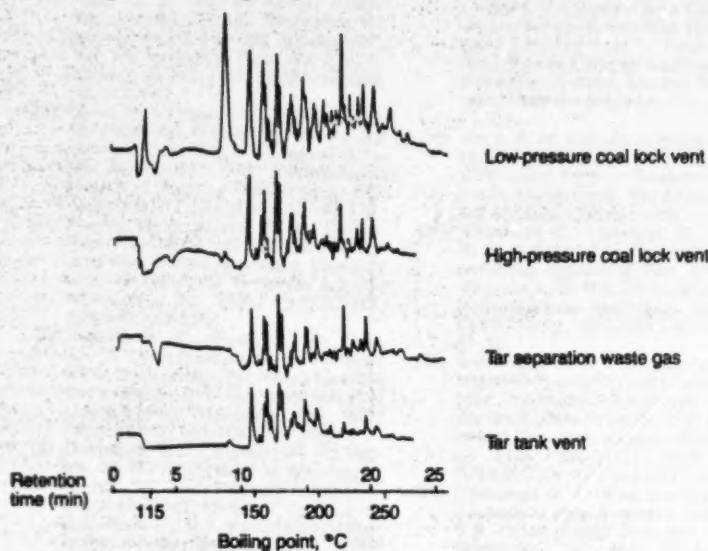
Organics profiles

A major deficiency of the detailed analysis data from these complex coal gasification streams is that they are incomplete; only a portion of the total organics has been identified and quantified. Without a costly effort, such complex mixtures cannot be identified and quantified, and comparisons between similar streams from different processes are questionable when only a small portion of a sample is included in the quantitative data.

Nevertheless, a technique known as "fingerprinting" (20, 21, 24) was used in the Kosovo study to compare organics from different sources and was found to be useful and cost effective. One of the simplest methods for taking a fingerprint involves the use of a gas chromatogram developed with the aid of a flame ionization detector. A more definitive fingerprint can be obtained with an element-specific detector that provides profiles of the sulfur- or nitrogen-bearing components (Figure 3).

The similarity of the profiles in Figure 3 clearly indicates the presence of similar arrays of nitrogen-bearing components, which were identified tentatively as pyridine, alkyl pyridines, quinoline, and alkyl quinolines. When the selectivity provided by the element-specific detector was combined with fractionation by acid, base, and neutral

FIGURE 3
Chromatograms of nitrogen species*



*In condensates from four Kosovo streams.
Source: Reference 20.

extraction, organic groups were observed that were not detected by other detailed analyses. Base extractables (phenols, carboxylic acids, and mercaptans) that contained nitrogen, and acid extractables (amines and nitrogen heterocyclics) that contained sulfur (e.g., thiazoles) were among the previously undetected groups. Profiles of nitrogen- and sulfur-bearing species in stream condensates and in by-product fractions provide information about these organics that might not have been supplied by the detailed analyses.

These selective profiles indicate that multifunctional compounds such as thiazoles, oxazoles, and hydroxypyridines may be present in Kosovo organics and may indeed be present in the organics from other fixed-bed gasifiers. Because certain classes of organic compounds are not readily detected by GC/MS and must be specifically sought, they may have been present but not detected by the detailed analyses of the Chapman and FW/STOIC organics. In future work, searching techniques should be used to detect unrecognized classes of compounds.

Similarities in composition

The organics originating in the crude gas of fixed-bed gasification processes were broadly similar in composition. No gasifier showed a trend toward the production of any specific compound, hazardous species, or nonhazardous species that was different from the others.

Organics originating in the crude gas

of a coal gasification process can enter the environment either by escaping from the process through a discharge stream or a leak or by contributing to the level of pollutants in combustion flue gas. The impact of organics escaping to the environment is a process- and stream-specific problem because the composition of the organics is influenced by temperature and by contact with both aqueous and organic solvents.

Process operations such as aqueous scrubbing, selective gas cleaning, and selective water cleaning alter organic composition considerably. Lyophilic components are enriched in the light oils, hydrophilic components are concentrated in crude phenol, and both types of compounds are concentrated to some extent in the thermally condensed tar. As a result, the substance affecting the environment depends not only on what is produced in the gasifier but also on what occurs downstream to alter the mixture and possibly enrich compounds of concern in a transport medium.

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